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Spectroscopic analysis on the structure of poly methylmethacrylate (PMMA)

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Abstract The present work is devoted to the study of the structure and potential energy distribution of crystalline Poly Methylmethacrylate(PMMA) A qualitative analysis of the pure sample of PMMA has been made by a satisfactory vibration band assignment using FTIR and Raman spectra. A normal coordinate analysis has been carried out using the method of kinetic constants A systematic set of potential constants have been computed using the method of kinetic constants on the basis of C_s symmetry comparing with those of the related molecules The potential energy distribution confirms the correctness of the assignments made

Keywords Poly methylmethacrylate (PMMA), FTIR and Raman spectra, normal coordinate analysis

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1. Introduction

PMMA is an glassy polymer commercially called acrylic, with an amorphous structure, derived from the monomer methyl methacrylate. It is optically active [1] with high level of transparency and an excellent substitute for glass with good mechanical property. It is one of the hardest thermoplastics and is also scratch resistant. It is used for making attractive sign boards, optical fibers, contact lens, lighting fixtures, window screens, automobile lighting biological specimen, preservation dentures, syringes *etc.* Earlier works reported are on IR studies on automobile scrapyard, acrylic[2], optical fibre transmission studies using PMMA[3] and non-destructive analysis of photo-degradation of PMMA[4]. However, the vibrational spectra of PMMA have not been examined thoroughly so far, perhaps due to the high complexity and low symmetry of the monomers. In an attempt is made to identify the vibrational frequencies corresponding to each of the functional groups and hence forth its structural elucidation.

2. Experimental

The sample of Poly Methyl Methacrylate (PMMA) was procured from CIPET, Chennai, India. The Fourier transform Infrared spectra was recorded in the range 4000 - 400 cm^{-1} using Perkin Elmer spectrophotometer at Medopharm, Chennai , India The Laser Raman spectra in the same wave number range was recorded at RSIC, Chennai using the DILOR Z 24 Raman spectrophotometer. The spectra are presented in Figures 1 and 2.

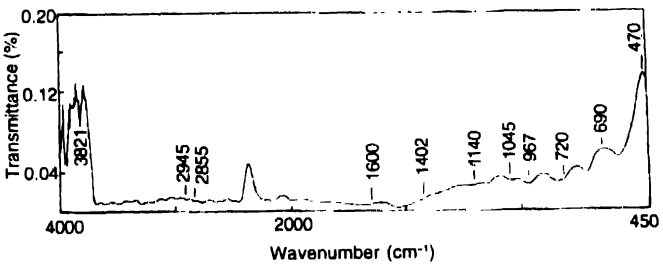

Figure 1. FTIR spectrum of poly methyl methacrylate

3. Normal coordinate analysis

The repeating unit of PMMA belongs to C_s symmetry [5]. The assumed structure of the compound under study is presented in Figure 3.The interatomic distances and bond angles were taken from Sutton Tables [6] from related compounds. PMMA has 39 fundamental modes of vibration under C_s point group

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and can be represented as $\Gamma_{vib} = 25A' + 14A''$. Of this, 22

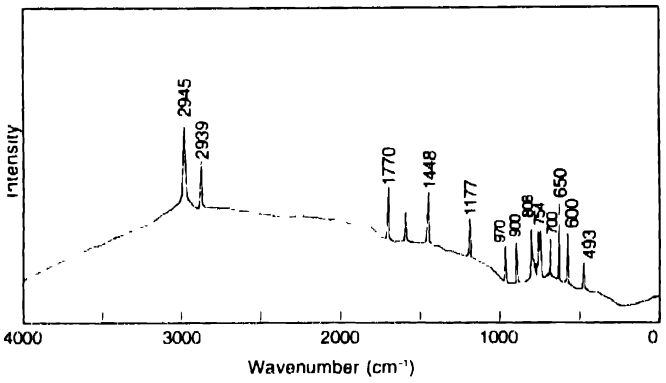

Figure 2. Laser Raman spectrum of poly methyl methacrylate

symmetric coordinates are considered here. 14 symmetric coordinates are assigned to A' species and 8 to A" species. In view of the C_s symmetry, the monomers of the polymer will have only two types of vibrations, namely, stretching and bending and will be active in both IR and Raman. On the basis of internal coordinates, ΔD, Δd_1, Δd_2, ΔL, Δl_1, Δl_2, Δr_1, Δr_2, ΔR_1, ΔR_2, ΔR_3, Δh_1, Δh_2, Δh_3, $\Delta \Phi_1$, $\Delta \Phi_2$, $\Delta \Phi_3$,

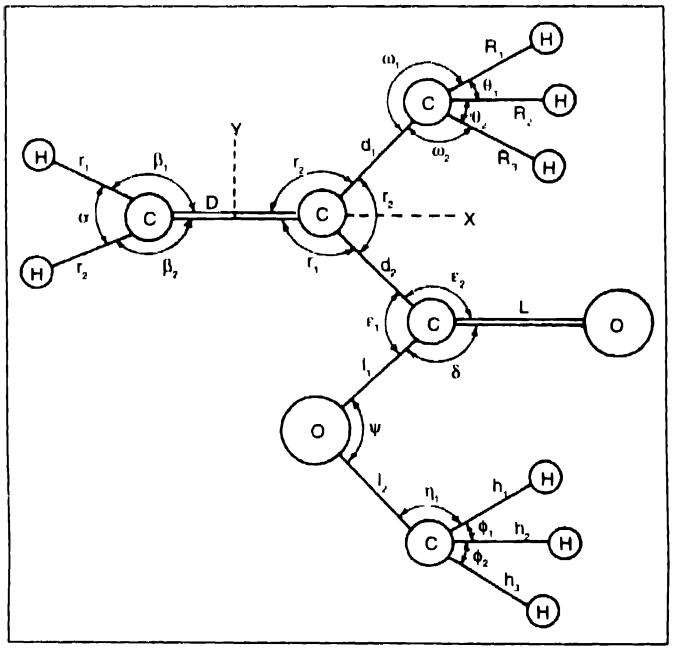

Figure 3. Structure of polymethyl methacrylate.

$\Delta\theta_1$, $\Delta\theta_2$, $\Delta\theta_3$, $\Delta\beta_1$, $\Delta\beta_2$, $\Delta\alpha$, $\Delta\gamma_1$, $\Delta\gamma_2$, $\Delta\gamma_3$, $\Delta\omega_1$, $\Delta\omega_2$, $\Delta\omega_3$, $\Delta\eta_1$, $\Delta\eta_2$, $\Delta\eta_3$, $\Delta\xi_1$, $\Delta\xi_2$, $\Delta\delta$ and $\Delta\psi$ are the orthonormal set of symmetric coordinates constructed for in plane and out of plane vibrations[7,8] that are used in the present work. A normal coordinate analysis has been carried out using the method of kinetic constants[9-11].The symmetric coordinates are listed below :

A' species:

$S_1 = \Delta D$, $S_2 = (1/\sqrt{2})(\Delta d_1 + \Delta d_2)$, $S_3 = \Delta L$, $S_4 = (1/\sqrt{2})(\Delta l_1 + \Delta l_2)$, $S_5 = \Delta\alpha$, $S_6 = (1/\sqrt{2})(\Delta\gamma_1 + \Delta\gamma_2)$, $S_7 = \Delta\psi$, $S_8 = (1/\sqrt{3})(\Delta R_1 + \Delta R_2 + \Delta R_3)$, $S_9 = (1/\sqrt{3})(\Delta h_1 + \Delta h_2 + \Delta h_3)$, $S_{10} = \Delta\gamma_3$, $S_{11} = (1/\sqrt{3})(\Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3)$, $S_{12} = (1/\sqrt{3})(\Delta\eta_1 + \Delta\eta_2 + \Delta\eta_3)$, $S_{13} = (1/\sqrt{2})(\Delta r_1 + \Delta r_2)$, $S_{14} = (1/\sqrt{2})(\Delta\xi_1 + \Delta\xi_2)$

A" species :

$S_{15} = (1/\sqrt{2})(\Delta d_1 - \Delta d_2)$, $S_{16} = (1/\sqrt{2})(\Delta l_1 - \Delta l_2)$, $S_{17} = (1/\sqrt{2})(\Delta\gamma_1 + \Delta\gamma_2)$, $S_{18} = (1/\sqrt{6})(2\Delta\theta_1 - \Delta\theta_2 + \Delta\theta_3)$, $S_{19} = (1/\sqrt{6})(2\Delta R_1 - \Delta R_2 + \Delta R_3)$, $S_{20} = (1/\sqrt{6})(2\Delta h_1 - \Delta h_2 + \Delta h_3)$, $S_{21} = (1/\sqrt{2})(\Delta\xi_1 - \Delta\xi_2)$, $S_{22} = \Delta\delta$

3.1 IR and Raman vibrational band assignment :

The C-H asymmetric stretching of methyl and methylene groups are expected to occur in the range 3100–2950 cm^{-1} and symmetric stretching[12] between 2900–2840 cm^{-1}. In PMMA the symmetric stretching vibrations are assigned to the bands at 2837, 2855 and 2867 cm^{-1} for IR and 2839 and 2880 cm^{-1} for Raman and asymmetric stretchings at the same values for both the spectra *i.e.*, at 2905 and 2945 cm^{-1}. The symmetric vibrations appear to be intense. In PMMA, most of the IR and Raman bands are found at about the same values, the C-C stretchings occurs well at the expected value, *i.e.*, symmetric stretching at 967 cm^{-1} and asymmetric stretching at 1087 cm^{-1}[13] The H-C-O bending vibrations is expected at 1160 cm^{-1} for the hydrogen substituted ethylene compounds[14]. The vibrations at 1140 cm^{-1} may be due to this bending.The methylene bending occurs with high intensity at 1370 cm^{-1} [15] . The CCC deformation vibration [15] is observed for PMMA at 755 and 864 cm^{-1} The symmetric deformation vibration of CCO is observed at 579 cm^{-1} and asymmetric at 721 cm^{-1} .This however has occurred at the expected value [14]. The C-O symmetric and asymmetric stretching vibrations [14] occur between 1030-1200 cm^{-1}. In the case of di and tri substituted ethane compounds, the bands at 1045 cm^{-1} and 1118 cm^{-1} are assigned to the symmetric and asymmetric C-O stretching vibrations.

3.2 Computational method :

A computational procedure is developed to find the B Matrix G Matrix and then the K matrix as the inverse of the G matrix by using Gauss- Jordon algorithm[16].The Crout algorithm[17] is modified to evaluate the determinant value of $(F*G - \lambda*E)$ matrix. For different F_{ij}, the corresponding F_{ii} are obtained by

Table 1. Normal modes of vibration, potential constants and PED of poly methyl methacrylate

Fundamental modes	Frequencies cm^{-1} FTIR	Laser Raman	Assignment	Potential constants (10^2N/m)	PED %
ν_1 (A')	967 (s)	970 (ms)	ν_s C-C	6 8138	99
ν_2 (A')	1010 (s)	–	ν_s C-C	6 8143	97
ν_3 (A')	1730 (vs)	1770 (ms)	ν_s C=O	6 6756	52
ν_4 (A')	1045 (s)	1055 (w)	ν_s C-O	6 3247	96
ν_5 (A')	1370 (s)	–	δ_s CH_2	0 5140	85
ν_6 (A')	755 (s)	754 (ms)	δ_s CCC	0 5063	42
ν_7 (A')	650 (ms)	650 (s)	δ COC	0 5219	40
ν_8 (A')	2837 (vs)	2839 (ms)	ν_s CH_3	5 8722	98
ν_9 (A')	2855 (vs)	–	ν_s CH_3	5 8716	98
ν_{10} (A')	820 (s)	808 (ms)	δ_{as} CCC	0 5070	48
ν_{11} (A')	1385 (s)	–	δ_s HCH	0 5161	40
ν_{12} (A')	1140 (vs)	1177 (s)	δ OCH	0 4928	56
ν_{13} (A')	2867 (vs)	–	ν_s C-H	5.8732	98
ν_{14} (A')	579 (s)		δ_s OCC	0 4957	41
ν_{15} (A")	1087 (s)	–	ν_{as} C-C	6.2744	99
ν_{16} (A")	1118 (s)	–	ν_{as} C-O	6 2753	98
ν_{17} (A")	864 (s)	900 (ms)	δ_{as} CCC	0 5081	44
ν_{18} (A")	1525 (vs)	1560 (s)	δ_{as} CH_3	0 4928	99
ν_{19} (A")	2905 (ms)	2903 (ms)	ν_{as} C-H	4 3425	93
ν_{20} (A")	2945 (s)	2945 (s)	ν_{as} C-H	4 3456	93
ν_{21} (A")	721 (vs)	700 (w)	δ_{as} OCC	0 4957	40
ν_{22} (A")	605 (s)	600 (w)	δ_{as} OCO	0 4824	41

w-weak, ms -medium strong , s-strong, vs-very strong

Wilson's approximation[18].PED is calculated using the relation % PED = $L_{ij}^2 F_{ij} / \lambda_j$. The frequencies of PMMA observed in both IR and Raman spectra with their relative intensities and probable assignments of fundamental modes are summarized in Table 1 along with a reliable set of potential constants and PED calculation.

4. Conclusion

A satisfactory vibrational band assignment has been made available for poly methyl methacrylate through Infrared and Raman spectral measurements. A systematic set of potential constants have been computed using the method of kinetic constants on the basis of C_s symmetry. To check whether the chosen set of symmetric coordinates contribute maximum to the potential energy associated with the normal coordinates of the molecules, the potential energy distribution has been carried out. The potential energy distribution for all the methyl and methylene stretching and bending modes were found to be especially very satisfactory[19] .

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